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(54) **PROCESS FOR HYDROLYTICALLY OBTAINING A CARBOXYLIC ACID AND ALCOHOL FROM  
THE CORRESPONDING CARBOXYLATE**

**VERFAHREN FÜR DIE HYDROLYTISCHE HERSTELLUNG EINER CARBONSÄURE UND EINES  
ALKOHOLS AUSGEHEND VOM ENTSPRECHENDEN CARBOXYLAT**

**PROCEDE PERMETTANT D'OBTENIR PAR HYDROLYSE UN ACIDE CARBOXYLIQUE ET DE  
L'ALCOOL A PARTIR D'UN CARBOXYLATE CORRESPONDANT.**

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**Description**Technical Field

- 5 **[0001]** The present invention relates to a process and to a device for the simultaneous hydrolytic cleavage of a carboxylate into the corresponding carboxylic and alcohol.

Background of the Invention

- 10 **[0002]** Carboxylates, especially low molecular weight carboxylates, occur in the chemical industry during various reactions as by-products or main products. For example, methyl acetate is a typical by-product in the production of purified polyvinyl alcohol. Methyl acetate mixtures from polyvinyl alcohol plants, besides a small amount of low-boiling substances such as acetaldehyde, contain an azeotropic mixture of methyl acetate and methanol.
- 15 **[0003]** For chemical companies, where methyl acetate as a by-product occurs in relatively small quantities, methyl acetate is not an economically interesting product, since it cannot be profitably sold on the market. A better price can be obtained if methyl acetate is hydrolysed into acetic acid and methanol. The hydrolysis can be carried out either as a batch process or continuously, by using either a reactor in conjunction with conventional distillation or a single reactive distillation column.
- 20 **[0004]** The use of a reactor in conjunction with a distillation column for the hydrolysis of methyl acetate is described, for example, in US 4,352,940. This type of hydrolysis of methyl acetate has several disadvantages: (a) since the reaction is an equilibrium reaction with a small equilibrium constant, the yield of reaction product is small, (b) because of the azeotropic mixture which is set up in the reaction mixture between methyl acetate/water, on the one hand, and methyl acetate/methanol, on the other, several distillation stages are needed after the reaction. This leads to high investment and running costs, (c) corrosion problems occur because homogeneous catalysts such as sulphuric and hydrochloric acid are used in the known conventional processes.
- 25 **[0005]** US 5,113,015 discloses a process for obtaining acetic acid from methyl acetate, in which methyl acetate and water are brought into contact in the presence of catalyst packing in a distillation column. In this case, the methyl acetate is hydrolysed into acetic acid and methanol. The resulting reaction mixture is in this case partially separated at the same time in the separation column.
- 30 **[0006]** US 5,770,770 likewise discloses a process for the hydrolysis of a methyl acetate mixture in a reactive distillation column. The hydrolysis of a methyl acetate flow, which contains more than 50% methyl acetate, takes place in a reaction zone in which ion exchange packing is present. The methyl acetate mixture is supplied from below to the ion exchange packing, and water from above onto the ion exchange packing. The unreacted methyl acetate and water vapour are collected and condensed in the upper part of the reaction zone, and are then recycled back to the reaction zone. At the same time, the base is collected and separated into the hydrolysis products and impurities. The impurities are then returned to the reaction zone.
- 35 **[0007]** Both aforementioned US patents, 5,113,015 and 5,770,770, teach the use of strongly acid ion exchangers as catalysts. In US 5,770,770, it is proposed to put the ion exchange material in the form of Raschig rings, by adding a plastic as binder to the ion exchanger and pressing the mixture into appropriate shapes. In US 5,113,015, the catalyst material is conserved in glass wool, and the mat formed therefrom is rolled up with a wire mesh between the layers, in order to promote circulation of the fluids. The catalyst packing material may be a compliant open-mesh substance, e.g. a metal cloth. Another usable material is a more rigid cellular monolith, which can be produced from steel, polymers or ceramic material. The catalyst packing material may, however, also be produced from corrugated metal sheets or corrugated plastic or ceramic plates.
- 45 **[0008]** The processes described above, which use only a single reactive distillation column, suffer from the fact that methyl acetate is only partially converted to methanol and acetic acid. The amount of methyl acetate in the product flow makes the use of at least one additional purification stage necessary, which leads to additional investment and running costs. A further problem is that the methyl acetate feed flow often contains metal ions, which poison the catalyst in the reactive distillation column. The replacement of the catalyst material in the distillation column by fresh material, however, is laborious and expensive. Furthermore, it is desirable for the hydrolysis process to be controlled - independently of the methyl acetate concentration in the feed flow - in such a way that, as required by the operator e.g. of a polyvinyl alcohol plant, the acetic acid obtained has a specific water content or is virtually anhydrous.
- 50 **[0009]** The object of the present invention is therefore to provide an improved process for the hydrolysis of a carboxylate, especially methyl acetate, methyl formate and allyl acetate, by using a reactive distillation column. In particular, it is desirable to improve the conversion ratio of carboxylates into alcohol and carboxylic acid. A further object is to prevent poisoning of the catalyst used in the distillation column. Another object is to optimise the energy budget of the process. It is also intended to offer a process and a hydrolysis device, which allow great flexibility in terms of composition and quantity of the feed. The composition of the product flows is also intended to be controllable in a large
- 55

range by the process. A further object is to improve the conversion ratio of methyl acetate into acetic acid and methanol.

#### Description

**[0010]** According to the invention, this is achieved in the case of a process according to the precharacterising clause of Claim 1, in that the feed containing the carboxylate is firstly fed into a pre-reactor, in which the carboxylate is brought into contact with a first catalyst in the presence of water, by means of which the carboxylate is partially cleaved into the hydrolysis products. The reaction mixture from the pre-reactor is fed into the reactive distillation column, and is brought into contact with a second hydrolysis catalyst for at least partial conversion of the remaining carboxylate into the corresponding carboxylic acid and alcohol. The process according to the invention has the surprising advantage that a substantially higher conversion ratio can be achieved than with known processes. A further advantage is that, by the use of a pre-reactor, the working life of the reactive distillation column can be substantially lengthened, since catalyst poisons, e.g. metal ions, are predominantly trapped in the pre-reactor. A further advantage is that, by the pre-reactor, differences or fluctuations in the feed quantity or in the mixture composition can be compensated. Yet another advantage is that the particle size of the catalyst material used in the pre-reactor plays a less important role than in the case of the catalyst packings advantageously used in the reactive distillation column. Batches with a specific particle size are normally used for catalyst packings, since the catalyst material could not otherwise be fully retained by the partially permeable packing walls.

**[0011]** Advantageously, at least the head flow of the reactive distillation column or the base flow is delivered to at least one further separation stage, and is at least partially separated into the components. One or more downstream separation stages are preferably used if the resulting reaction mixture is to be separated as fully as possible into the individual components.

**[0012]** Advantageously, the carboxylate flow is mixed with at least an equimolar amount of water, and the carboxylate/water mixture is fed into the pre-reactor. The molar ratio between carboxylate and water is expediently between approximately 1:1 and 1:15, preferably between 1:2 and 1:10, and more particularly preferably between 1:4 and 1:7. The hydrolysis proceeds particularly well if the carboxylate/water ratio in the feed flow is between 1:3 and 1:5.

**[0013]** Although the hydrolysis reaction can actually be carried out at room temperature, the carboxylate/water mixture is preferably heated to a temperature of between 30 and 100°C, preferably from 40 to 90°C, and more particularly preferably between 50 and 80°C, since the reaction proceeds well and quickly at these temperatures. The reaction mixture from the pre-reactor is expediently fed into the reactive distillation column in the region either where the catalyst is arranged, or slightly above or below this region. The head flow containing alcohol, water, carboxylate and volatile components may be delivered to a further separation stage, preferably a distillation column, in which the mixture is further separated.

**[0014]** Particularly advantageously, the reactive distillation column is operated in such a way that the carboxylic acid and at least one part of the water remain in the base of the reactive distillation column. In this case, the reaction mixture from the pre-reactor is preferably introduced into the reactive distillation column at a point above the catalyst zone centre. The base flow produced, which essentially contains alcohol, water and carboxylic acid, may be delivered to a further separation stage, preferably a distillation column, in which the mixture is further separated. It is also conceivable for both the head flow and the base flow of the reactive distillation column to be delivered to further separation stages, e.g. distillation columns, and separated. As a variant, the head product may be delivered partially to the pre-reactor or to the feed flow of the reaction column, in order to further convert carboxylate contained in the head flow. Such recycling of the head flow of the reactive distillation column allows the capacity of the plant to be increased substantially.

**[0015]** Advantageously, the reactive distillation column is operated in such a way that the added water and the volatile components are essentially contained in the head flow. This has the advantage that the carboxylic acid is produced in the base with a proportion by weight > 95%, preferably > 99%. The highest conversion ratio can in this case be achieved if the reaction mixture from the pre-reactor is introduced into the reactive distillation column at a point below the catalyst zone centre.

**[0016]** The process according to the invention is advantageously operated continuously, i.e. carboxylate and water or a mixture thereof, respectively, are continuously fed into the pre-reactor, and the resulting reaction mixture is drawn off continuously from the pre-reactor and fed into the reactive distillation column, where unreacted carboxylate is for the most part converted into its hydrolysis products, the hydrolysis products being drawn off continuously as a head flow or as a bottom fraction (base flow), and optionally delivered to a further separation stage. The volume flow delivered per unit volume of catalyst is advantageously between 0-15 h<sup>-1</sup>, preferably 0.5-8 h<sup>-1</sup> and particularly preferably between 1-4 h<sup>-1</sup>.

**[0017]** The present invention also relates to a reaction and separation device according to the precharacterising clause of Claim 16, characterised by at least one pre-reactor having at least one inlet and one outlet for respectively supplying and discharging a fluid flow comprising the carboxylate or the carboxylate mixture into the pre-reactor and therefrom, respectively, a first catalyst, which is arranged or deposited in the pre-reactor, a connecting line, which

connects the outlet of the pre-reactor to the inlet of the reactive distillation column, and first heating means for heating the fluid flow or the pre-reactor. The advantages of this device according to the invention have already been mentioned in connection with the description of the process. Advantageous refinements of the device are described in the dependent claims.

5 **[0018]** As a result of the fact that the pre-reactor is arranged approximately vertical, and the inlet is located at the top and the outlet at the bottom, the catalyst material in the pre-reactor experiences vortexing, since the flow direction of the reaction flow and gravity keep the catalyst material at the bottom of the pre-reactor. It is thereby possible to prevent undesired attrition of the catalyst material. It is also conceivable for the inlet and outlet to be provided laterally on opposite sides above or below the catalyst zone, respectively. It is in principle also conceivable for the inlet to be arranged at the bottom and the outlet at the top.

10 **[0019]** In a particularly preferred embodiment, two pre-reactors or one pre-reactor having two reaction chambers are used, and means are provided for making it possible to send the feed flow respectively through one of the pre-reactors or one of the reaction chambers, so that the other pre-reactor or the other reaction chamber, respectively, can be provided with fresh catalyst. This has the advantage that the device can be operated continuously for a long period of time. It is also conceivable to arrange the two pre-reactors one behind the other. Such an arrangement has the advantage that different temperatures can be maintained in the two reactors, in order to positively exploit the dependency of the equilibrium reaction on temperature (e.g. 1st reactor is operated at a higher temperature than 2nd reactor). According to an advantageous processor variant, the flow leaving the pre-reactor may be partially returned to the pre-reactor. This has the advantage that the pre-reactor can be dimensioned smaller than if no recycling line is provided around the pre-reactor, and the capacity of the plant is variable in a larger range. Yet another advantage is that phase separation in the feed to the pre-reactor can be avoided by a recycled flow.

15 **[0020]** Expediently, the reactive distillation column has a catalyst zone and one lower and one upper rectification zone, the upper rectification zone being provided above the catalyst zone and the lower rectification zone being provided below the catalyst zone. The rectification zone may have separating stages, Raschig rings, structured material exchange packings etc.

20 **[0021]** The pre-reactor is advantageously designed as a tube, in which the first catalyst is deposited. Expediently, the first and second catalysts are acid solid-state catalysts, the first catalyst having a particle size of between approximately 0.35 and 3 mm and the second catalyst having one between approximately 0.5 and 1.5 mm, preferably 0.63 and 1 mm, and more particularly preferably between 0.7 and 1 mm. While the first catalyst is preferably present as a bed in the pre-reactor in the form of spheres, rings, extrudates etc., the second catalyst is advantageously introduced into the reactive distillation column as so-called structured catalyst packing. Suitable structured catalyst packings are described, for example, in US 5,417,939 (Shelden), US 5,470,542 (Stringaro) and US 5,536,699 (Gheffi), the content of which is hereby included by reference. The term structured catalyst packing should be understood to mean a structure having retaining devices (e.g. bags) for solid catalyst material and having flow channels, which are present in the structure. It is also conceivable to use such structured catalyst packings both in the pre-reactor and in the reactive distillation column.

25 **[0022]**

40 Figure 1 diagrammatically shows a first embodiment of a device for the catalytic hydrolysis of carboxylates, with a pre-reactor and a reactive distillation column;

Figure 2 diagrammatically shows a second embodiment of a device for the catalytic hydrolysis of carboxylates, with a pre-reactor, a reactive distillation column and a distillation column for further separation of the bottom fraction of the reactive distillation column;

45 Figure 3 diagrammatically shows a third embodiment of a device for the catalytic hydrolysis of carboxylates, with a pre-reactor, a reactive distillation column and a distillation column for further separation of the head flow of the reactive distillation column;

Figure 4 diagrammatically shows a fourth embodiment of a device for the catalytic hydrolysis of carboxylates, with two pre-reactors;

50 Figure 5 diagrammatically shows a fifth embodiment of a device for the catalytic hydrolysis of carboxylates, with two pre-reactors, the feed from the pre-reactors being fed into the reactive distillation column at different points.

55 **[0023]** The device 11 for the simultaneous catalytic hydrolysis of a carboxylate, especially methyl acetate, methyl formate or allyl acetate, into the hydrolysis products and at least partial separation of the reaction mixture, comprises essentially a pre-reactor 13 and a reactive distillation column 15, which are connected to one another by a connecting line 17.

**[0024]** The pre-reactor 13 has an inlet 19 for feeding a fluid flow into the reactor space and an outlet 21 for drawing off the reaction mixture. The connecting line 17 connects the outlet 21 of the reactor to an inlet 23 on the reactive distillation column 15. The pre-reactor 13 is preferably tubular, the inlet 19 and the inlet [sic] 21 being arranged on

opposite end sides of the tube. The pre-reactor 13 has a catalyst bed 25 of a solid first catalyst material.

[0025] The reactive distillation column 15 has a catalyst zone 27 and an upper and lower rectification zone 29, 31, which are provided respectively below and above the catalyst zone 27. A second solid-state catalyst 33, preferably contained in so-called catalyst packing, is provided in the catalyst zone 27. The rectification zones are formed in a known way e.g. by Raschig rings, column stages, structured (material exchange) packings etc. A line 35 for drawing off the base flow is provided at the column foot, and a line 37 for drawing off the head flow of the reactive distillation column 15 is provided at the column head. The line 35 is in connection by means of a line 39 with a heat exchanger 41, which is connected via a line 43 in turn to the column foot. The heat exchanger 41 is used to heat the column base. By means of a branch line 44, part of the base can be removed as a base or base [sic] flow from the hydrolysis and separation device.

[0026] The line 37 for the head flow leads to a condenser 45, by which the gaseous head flow can be liquefied. By means of a recycling line 47 connected to the condenser, part of the distillate can be returned as recycle to the reactive distillation column 15. Part or all of the distillate from the reactive distillation column 15 can be removed via the line 49.

[0027] The carboxylate compound to be hydrolysed can be delivered into the pre-reactor 13 via a line 51, which is connected to the inlet 19. Water can be added to the line 51 via a line 53. The carboxylate/water mixture can be heated by a heat exchanger 55, which is in connection with the line 51.

[0028] The second illustrative embodiment (Fig. 2) differs from the first in that a distillation column 57 is connected to the line 44, which is in connection with the column foot. For the sake of simplifying the description, the same reference numbers as in the description of the first illustrative embodiment are therefore used for identical parts, and the description is limited to the additional features of the second illustrative embodiment.

[0029] Like the reactive distillation column 15, the distillation column 57 also has a heat exchanger 61, integrated in a circulation line 59, in order to heat the base of the distillation column 57. Part of the distillation base can be removed from the hydrolysis device by a branch line 63.

[0030] At the head of the distillation column 57, a condenser 65 is connected by means of a line 67 to the column. The condensate can be returned via the line 69 into the distillation column, or can be removed via the line 71 from the hydrolysis and separation device.

[0031] The illustrative embodiment in Figure 3 differs from that in Figure 2 in that the distillation column 57 is connected to the line 49, which is in connection with the condenser 45 of the reactive distillation column. By means of the distillation column, the head flow, which may be a compound mixture, can be separated at least partially into the components. A further difference is that a recycling or recirculation line 73 is provided around the pre-reactor 13, in order to make it possible for part of the flow leaving the pre-reactor 13 to be delivered newly thereto. Depending on the separation problem, an extraction column may also be used instead of the distillation column.

[0032] The illustrative embodiment in Figure 4 has the distinguishing feature of two pre-reactors 13a and 13b, which can be used simultaneously or alternately. The reaction flow can in this case be fed through valves (not represented in further detail) either through the pre-reactor 13a or pre-reactor 13b. The use of two pre-reactors has the advantage of that, in the event that it is necessary to replace the catalyst material in one pre-reactor, operation need not be interrupted since the process flow can be fed through the other pre-reactor.

[0033] The illustrative embodiment in Figure 5 differs from that in Figure 4 in that the pre-reactors 13a and 13b are connected by means of separate lines 17a and 17b to the reactive distillation column 15. The line 17a is connected to an inlet 23a, and the line 17b to an inlet 23b. The inlet 23a is arranged in the region of the reaction zone or below the latter, and the inlet 23b in the region of the reaction zone or above the latter. The composition of the feed can be adjusted individually for each pre-reactor. The reaction conversion and the productivity can thereby be improved. In the case of using pure components, i.e. only water or only carboxylate, the use of a second pre-reactor may also be omitted.

[0034] The hydrolysis of a carboxylate will be described below with reference to the hydrolysis of methyl acetate as an example of other carboxylates. Methyl acetate flow having a proportion by weight of at least 50% methyl acetate is mixed with an amount of water at least equimolar with respect to methyl acetate, preferably a 4 to 7 times molar excess of water. The mixture is then heated by the heat exchanger 55, preferably to a temperature between 30 and 100°C, preferably 50 and 80°C, and fed into the preferably vertically arranged pre-reactor 13.

[0035] The pre-reactor 13 is packed with an acid solid-state catalyst, e.g. a cationic ion exchanger. The catalyst preferably has a particle size between approximately 0.35 to 3 mm. Such a catalyst material is available, for example, under the name Amberlyst 15 from the company Rohm and Haas. Alternative catalysts are, for example, zeolites, aluminium oxide, silicon oxide etc.

[0036] The methyl acetate/water mixture flows through the pre-reactor 13 in cocurrent from top to bottom, and comes into contact with the catalyst material during this. In this case, partial hydrolysis of the methyl acetate takes place. The conversion of the methyl acetate in the pre-reactor is between 20 and 100%, preferably between 50 and 80%, of the equilibrium conversion. The resulting reaction mixture is introduced via the line 17 into the catalyst zone 27 of the reactive distillation column 15, although the introduction may also take place above or below the catalyst zone. As a

variant, part of the reaction mixture may be recycled back to the pre-reactor 15 (Fig. 3).

**[0037]** The reactive distillation column 15 is preferably operated in such a way that the more volatile methyl acetate rises in the catalyst zone, and the less volatile water flows down over the catalyst as reflux. In this case, intense contact between catalyst material, water and methyl acetate takes place, in the course of which methyl acetate is cleaved into acetic acid and methanol.

**[0038]** Depending on the desired purity and/or composition of the acetic acid, the reactive distillation column may be operated in such a way that unreacted water collects together with the acetic acid in the base of the column (case 1) or is essentially contained in the head flow of the reactive distillation column (case 2). In the first case, an acetic acid/water/methanol mixture is produced, which can be further separated e.g. by a downstream separation stage (Fig. 2). In the second case, aqueous or essentially anhydrous acetic acid with a purity > 99% can be obtained.

**[0039]** The temperature of the pre-reactor, or of the reactive distillation column, respectively, may be established as a function of pressure, a certain overpressure making it possible to operate at a higher temperature.

**[0040]** In the process utilising the device in Figure 2, the head flow of the reactive distillation column contains methyl acetate, methanol, water and low-boiling components. The base, which contains methanol, water, acetic acid and traces of methyl acetate, is removed as a so-called base flow. The volume ratio between the head flow 37 and the base flow 35 varies between 1:1 and 1:1000, preferably 1:30 to 1:200. The reflux ratio of the reactive distillation column is between 1 and 300, and preferably between 80 and 200. The base flow 35 of the reactive distillation column can be further separated in the distillation column 57. The head flow of the distillation column 57, exiting through the line 67, contains methanol and traces of methyl acetate, and the base flow (line 59) consists essentially of aqueous acetic acid.

**[0041]** In the process utilising the device in Figure 3, the head flow of the reactive distillation column 15 contains methyl acetate, methanol, water and low-boiling components. The base flow contains either pure acetic acid, i.e. acetic acid at more than 99% proportion by weight, or aqueous acetic acid. The volume ratio between the base flow 35 and the head flow 37 preferably varies between 1:1 and 1:10, and more particularly preferably between 1:1 to 1:4. The reflux ratio of the reactive distillation column is between 1 and 100, and preferably between 5 and 50. The head flow of the reactive distillation column can be further separated in the distillation column 57. The head flow of the distillation column 57, exiting through the line 67, contains methanol, methyl acetate, water and low-boiling components. The base flow (line 59) contains essentially water.

Examples:

**[0042]** In the following experimental examples, a cationic solid-state catalyst from the company Rohm and Haas, Germany was used (Amberlyst CSP 2). In the reaction distillation column, the catalyst was introduced into structured catalyst cracking.

#### 1st Experiment (Prior Art)

**[0043]** A single reactive distillation column was used. The base flow contained a mixture of methyl acetate, methanol, acetic acid and water, which was separated in an additional purification column into a methyl acetate/methanol mixture and an acetic acid/water mixture.

**[0044]** The methyl acetate flow to be hydrolysed had the following composition (in per cent by weight):

|                |       |
|----------------|-------|
| acetaldehyde   | 0.4%  |
| methyl acetate | 98.3% |
| methanol       | 1.3%  |

#### [0045]

| Reactive Distillation Column: |                           |
|-------------------------------|---------------------------|
| inner diameter                | 220 mm                    |
| rectification zone            | 7 theoretical stages (TS) |
| reaction zone                 | 6 TS                      |
| stripping zone                | 8 TS                      |

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| Feed Flows:    |            |
|----------------|------------|
| methyl acetate | 35.87 kg/h |
| water          | 62.33 kg/h |

| Product Flows: |            |
|----------------|------------|
| head flow      | 0.67 kg/h  |
| base flow      | 97.87 kg/h |

| Experimental Conditions:   |          |
|----------------------------|----------|
| head pressure              | 956 mbar |
| feed point                 | 13 TS    |
| reflux ratio               | 220      |
| heat exchanger temperature | 73.7°C   |

| Result:                   |       |
|---------------------------|-------|
| methyl acetate conversion | 79.2% |

composition base flow of the reactive distillation column in per cent by weight:

|                |        |
|----------------|--------|
| methyl acetate | 6.97%  |
| methanol       | 14.19% |
| water          | 56.61% |
| acetic acid    | 22.24% |

## 2nd Experiment: Combination of Pre-reactor with Reac

### tive Distillation Column

**[0046]** A combination of pre-reactor with reactive distillation column was used. The base flow of the reactive distillation column contains methanol, acetic acid, water and traces of methyl acetate. This mixture was separated in a distillation column into a methanol flow containing traces of methyl acetate and an acetic acid/water mixture.

**[0047]** The methyl acetate flow to be hydrolysed had the following composition (in per cent by weight):

|                |        |
|----------------|--------|
| acetaldehyde   | 0.001% |
| methyl acetate | 96.53% |
| methanol       | 3.46%  |

| Reactive Distillation Column: |                           |
|-------------------------------|---------------------------|
| inner diameter                | 220 mm                    |
| rectification zone            | 7 theoretical stages (TS) |
| reaction zone                 | 6 TS                      |
| stripping zone                | 8 TS                      |

| Feed Flows:    |            |
|----------------|------------|
| methyl acetate | 38.61 kg/h |

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(continued)

| Feed Flows: |            |
|-------------|------------|
| water       | 58.20 kg/h |

| Product Flows: |            |
|----------------|------------|
| head flow      | 1.0 kg/h   |
| base flow      | 92.92 kg/h |

| Experimental Conditions:   |          |
|----------------------------|----------|
| head pressure              | 967 mbar |
| feed point                 | 13 TS    |
| reflux ratio               | 122      |
| heat exchanger temperature | 83.7°C   |

| Result:                   |       |
|---------------------------|-------|
| methyl acetate conversion |       |
| after pre-reactor         | 57.6% |
| overall                   | 98.0% |

composition base flow of the reactive distillation column in per cent by weight:

|                |        |
|----------------|--------|
| methyl acetate | 0.01%  |
| methanol       | 18.93% |
| water          | 50.54% |
| acetic acid    | 30.68% |

**[0048]** Example 3: simulation of the hydrolysis and separation reaction by means of the simulation program PRO/II of the company SIMSCI (Simulation Sciences Inc.) with the aim of obtaining pure acetic acid from a methyl acetate flow utilising a pre-reactor/reactive distillation column combination according to the invention:

| Reactive Distillation Column:  |                            |
|--|----------------------------|
| rectification zone   | 10 theoretical stages (TS) |
| reaction zone  | 25 TS                      |
| stripping zone   | 15 TS                      |
| For the methyl acetate flow to be hydrolysed, the following composition was assumed (in per cent by weight): |                            |
| acetaldehyde   | 0.9%                       |
| methyl acetate   | 93.1%                      |
| methanol   | 2.1%                       |
| water  | 3.9%                       |

| Feed Flows (in kg/h): |  |
|-----------------------|--|
| feed flow             | 6500 kg/h (of acetaldehyde, MeAc, MeOH and H <sub>2</sub> O) |
| water                 | 7100 kg/h  |



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## Product Flows (in kg/h):

|           |             |
|-----------|-------------|
| head flow | 10,000 kg/h |
| base flow | 3600 kg/h   |

## Experimental Conditions:

|                            |         |
|----------------------------|---------|
| head pressure              | 1.5 bar |
| feed point                 | 35 TS   |
| reflux ratio               | 10      |
| heat exchanger temperature | 120°C   |

## Result:

|  |       |
|--|-------|
| methyl acetate conversion:   |       |
| after pre-reactor  | 57.6% |
| overall  | 73.3% |
| base flow composition of the reactive distillation column in per cent by weight: |       |
| methyl acetate   | 0.00% |
| methanol   | 0.00% |
| water  | 0.01% |
| acetic acid  | 99.9% |

**[0049]** The process according to the invention is suitable, in particular, for the hydrolysis of low molecular weight esters (esters with C1 to C4 or higher alcohols), e.g. methyl acetate, methyl formate and allyl acetate.

**[0050]** Allyl alcohol can inter alia be produced by the hydrolysis of allyl acetate. The hydrolysis is in this case carried out according to known conventional methods in the presence of mineral acids or ion exchangers as catalyst.

**[0051]** The production of formic acid likewise takes place by a hydrolysis reaction. In this case, methyl formate is reacted with excess water to give formic acid and methanol. The reaction can in this case be carried out autocatalysed by formic acid (DE-A-44 449 79) or in the presence of acid catalyst, e.g. ion exchanger (DE-A-42 373 39). The processing of the hydrolysis products conventionally takes place with separation methods such as distillation, extraction, etc.

## Legend

### [0052]

- 11 hydrolysis device
- 13 pre-reactor
- 15 reactive distillation column
- 17 connecting line
- 19 pre-reactor inlet
- 21 pre-reactor (13) outlet
- 23 R.D. column inlet
- 25 catalyst bed
- 27 catalyst zone
- 29 lower rectification zone
- 31 upper rectification zone
- 33 solid-state catalyst
- 35 R.C. foot line
- 37 R.C. head line
- 39 line between line 35 and heat exchanger
- 41 column foot heat exchanger
- 43 line between heat exchanger and column foot
- 45 branch line

- 47 recycling line
- 49 line
- 51 feed line for carboxylate
- 53 water
- 5 55 heat exchanger before the pre-reactor (13)
- 57 distillation column
- 59 circulation line
- 61 heat exchanger for base of the distillation column
- 63 branch line
- 10 65 condenser
- 67 line between distillation column and condenser
- 69 line between condenser and distillation column
- 71 line for the removal of the distillate

# Claims

1. Process for hydrolytically obtaining a carboxylic acid and alcohol from the corresponding carboxylate and water, in which process a flow containing carboxylate is brought into contact with a hydrolysis catalyst in the presence of water at elevated temperature in a reactive distillation column (15), by means of which the carboxylate is at least partially hydrolysed into the carboxylic acid and alcohol, and the resulting reaction mixture is simultaneously separated at least partially into the components in the reactive distillation column, the more volatile compounds, e.g. alcohol, being drawn off from the head of the reactive distillation column (15) as a so-called head flow and the less volatile compounds, e.g. carboxylic acid, collecting at least partially in the base of the column (15) as a bottom fraction, which can be drawn off as a so-called bottom or base flow, further **characterised in that**
  - the flow containing the carboxylate is firstly fed to a pre-reactor (13), in which the carboxylate is brought into contact with a first catalyst in the presence of water, by means of which the carboxylate is partially cleaved into the hydrolysis products;
  - the reaction mixture is drawn off from the pre-reactor (13) and at least partially fed into the reactive distillation column (15), and is brought into contact with a second hydrolysis catalyst for at least partial conversion of the remaining carboxylate into carboxylic acid and alcohol.
2. Process according to Claim 1, **characterised in that** at least the head flow of the reactive distillation column (15) or the base flow is delivered to at least one further separation stage, and is at least partially separated into the components.
3. Process according to Claim 1 or 2, **characterised in that** the carboxylate is mixed with at least an equimolar amount of water, and the carboxylate/water mixture is fed into the pre-reactor (13).
4. Process according to one of Claims 1 to 3, **characterised in that** the molar ratio of carboxylate and water is between approximately 1:1 and 1:15, preferably between 1:2 and 1:10, and more particularly preferably between 1:4 and 1:7 or 1:3 and 1:5, respectively.
5. Process according to one of Claims 1 to 4, **characterised in that** the carboxylate/water mixture is heated to a temperature of between 30 and 100°C, preferably from 40 to 90°C, and more particularly preferably between 50 and 80°C.
6. Process according to one of Claims 1 to 5, **characterised in that** the reaction mixture from the pre-reactor (13) is fed into the reactive distillation column (15) in the region where the catalyst is arranged.
7. Process according to one of Claims 1 to 6, **characterised in that** the reactive distillation column (15) is operated in such a way that the unreacted water and the volatile components are essentially contained in the head flow.
8. Process according to Claim 7, **characterised in that** the reaction mixture from the pre-reactor (13) is introduced into the reactive distillation column (15) at a point below the catalyst zone centre or a small distance below the catalyst zone.

9. Process according to Claim 7 or 8, **characterised in that** the head flow is delivered to a further separation stage, preferably a distillation or extraction column, in which the mixture is further separated.
- 5 10. Process according to one of Claims 1 to 9, **characterised in that** the reactive distillation column (15) is operated in such a way that the carboxylic acid and unreacted water remain in the base of the reactive distillation column (15).
11. Process according to Claim 10, **characterised in that** the reaction mixture from the pre-reactor (13) is introduced into the reactive distillation column (15) at a point above the catalyst zone centre or a small distance above the catalyst zone.
- 10 12. Process according to Claim 10 or 11, **characterised in that** the base flow of the reactive distillation column (15) is delivered to a further separation stage, preferably a distillation or extraction column, in which the mixture is further separated.
- 15 13. Process according to one of Claims 1 to 12, **characterised in that** the head flow and the base flow of the reactive distillation column (15) are delivered to a further separation stage, preferably one distillation or extraction column each, in which the respective mixture is further separated.
- 20 14. Process according to one of Claims 1 to 13, **characterised in that** the process is operated continuously, i.e. the carboxylate and the water or a mixture thereof, respectively, are continuously fed into the pre-reactor (13), and the resulting reaction mixture is drawn off continuously from the pre-reactor (13) and fed into the reactive distillation column (15), where unreacted carboxylate is for the most part converted into its hydrolysis products, the hydrolysis products being drawn off continuously as a head flow or as a base flow, and optionally delivered to a further separation stage.
- 25 15. Process according to one of Claims 1 to 13, **characterised in that** the ester compound is a methyl, ethyl, i- or n-propyl ester, i- or n-butyl ester, especially acetates thereof, or a mixture of the aforementioned ester compounds.
- 30 16. Use of a hydrolysis and separation device having at least one reactive distillation column (15), in particular for converting a carboxylate into the corresponding carboxylic acid and the corresponding alcohol and at least partial separation of the hydrolysis products into individual components, having:
  - at least one pre-reactor (13) having at least one inlet and one outlet for respectively supplying and discharging a fluid flow comprising the carboxylate into the pre-reactor (13) and therefrom, respectively;
  - 35 - a first catalyst, which is arranged or deposited in the pre-reactor (13);
  - first heating means (55) for heating the fluid flow or the pre-reactor (13);
  - a reactive distillation column (15) having an inlet (23), which is connected by means of a connecting line (17) to the outlet (21) of the pre-reactor (13), the reactive distillation column (15) having the following features:
    - 40 - a catalyst zone (27) comprising a second catalyst and at least one rectification zone (29 or 31), which is formed by distillation packing, Raschig rings, separating stages or the like;
    - lines (37, 35), connected respectively to the distillation column head and the distillation column foot, for drawing off a head flow and a base flow, respectively; and
    - 45 - second heating means (41) for heating the base of the reactive distillation column (15), for hydrolytically obtaining a carboxylic acid and alcohol from the corresponding carboxylate and water according to one of the claims 1 to 15.
- 50 17. Use according to Claim 16, **characterised in that** the pre-reactor (13) is arranged approximately vertically, the inlet (19) being arranged at the top and the outlet (21) at the bottom or, conversely, the outlet (21) being arranged at the top and the inlet (19) at the bottom.
- 55 18. Use according to Claim 16 or 17, **characterised in that** two pre-reactors (13a, 13b) or one pre-reactor (13) having two reaction chambers are used, and means are provided for making it possible to feed the supply flow respectively through one of the pre-reactors or one of the reaction chambers, so that the other pre-reactor (13) or the other reaction chamber, respectively, can be provided with fresh catalyst.
19. Use according to one of Claims 16 to 18, **characterised in that** the reactive distillation column (15) has a catalyst zone (27) and one lower and one upper rectification zone (29) and (31), respectively, the upper rectification zone

(31) being arranged above the catalyst zone (27) and the lower rectification zone (29) being arranged below the catalyst zone (27).

20. Use according to one of Claims 16 to 19, **characterised in that** the inlet of the reactive distillation column (15) is located in the region of the catalyst zone (27).
21. Use according to one of Claims 16 to 20, **characterised in that** the pre-reactor (13) is tubular, and the first catalyst is a bed of a solid catalyst.
22. Use according to one of Claims 16 to 21, **characterised in that** at least the second catalyst is formed as structured catalyst packing.
23. Use according to one of Claims 16 to 22, **characterised in that** the structured catalyst packing is formed by packing elements having cavities, the catalyst material being introduced into the cavities.
24. Use according to one of Claims 16 to 23, **characterised in that** the first and second catalysts are acid solid-state catalysts, e.g. ion exchange resins, the first catalyst having a particle size of between approximately 0.35 and 3 mm and the second catalyst having one between approximately 0.5 and 1.5 mm, preferably 0.63 and 1 mm, and more particularly preferably between 0.7 and 1 mm.

#### Patentansprüche

1. Verfahren zur hydrolytischen Gewinnung einer Carbonsäure und Alkohol aus dem entsprechenden Carbonsäureester und Wasser, bei welchem Verfahren ein Carbonsäureester enthaltender Strom mit einem Hydrolyse-Katalysator in der Gegenwart von Wasser bei erhöhter Temperatur in einer Reaktiv-Destillationskolonne (15) kontaktiert wird, wodurch der Carbonsäureester wenigstens teilweise in die Carbonsäure und Alkohol hydrolysiert wird und das entstehende Reaktionsgemisch in der Reaktiv-Destillationskolonne (15) zeitgleich wenigstens teilweise in die Komponenten getrennt wird, wobei die leichter flüchtigen Verbindungen, z.B. Alkohol, vom Kopf der Reaktiv-Destillationskolonne (15) als sog. Kopfstrom abgezogen und die schwerer flüchtigen Verbindungen, z.B. Carbonsäure, sich wenigstens teilweise im Sumpf der Kolonne (15) als Bodenfraktion sammeln, welcher als sog. Boden- oder Sumpfstrom abgezogen werden kann, **weiter gekennzeichnet dadurch**,
  - **dass** der den Carbonsäureester enthaltende Strom zuerst in einen Vorreaktor (13) geleitet wird, in welchem der Carbonsäureester in Gegenwart von Wasser mit einem ersten Katalysator kontaktiert wird, wodurch der Carbonsäureester teilweise in die Hydrolyseprodukte gespalten wird;
  - **dass** das Reaktionsgemisch aus dem Vorreaktor (13) abgezogen und wenigstens teilweise in die Reaktiv-Destillationskolonne (15) geleitet und mit einem zweiten Hydrolyse-Katalysator kontaktiert wird zwecks wenigstens teilweisen Umsetzung des verbleibenden Carbonsäureesters in Carbonsäure und Alkohol.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** wenigstens der Kopfstrom der Reaktiv-Destillationskolonne (15) oder der Sumpfstrom wenigstens einer weiteren Trennstufe zugeführt und wenigstens teilweise in die Komponenten aufgetrennt wird.
3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** der Carbonsäureester mit wenigstens einer äquimolaren Menge Wasser vermischt wird und das Carbonsäureester-/Wasser-Gemisch in den Vorreaktor (13) geleitet wird.
4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** das molare Verhältnis von Carbonsäureester und Wasser zwischen ungefähr 1:1 und 1:15, vorzugsweise zwischen 1:2 und 1:10 und ganz besonders bevorzugt zwischen 1:4 und 1:7 resp. 1:3 und 1:5 liegt.
5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** das Carbonsäureester-/Wasser-Gemisch auf eine Temperatur zwischen 30 und 100 °C, vorzugsweise 40 bis 90 °C und ganz besonders bevorzugt zwischen 50 und 80 °C erwärmt wird.
6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** das Reaktionsgemisch aus dem Vorreaktor (13) im Bereich, wo der Katalysator angeordnet ist, in die Reaktiv-Destillationskolonne (15) geleitet wird.

7. Verfahren nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** die Reaktiv-Destillationskolonne (15) so gefahren wird, dass das nicht umgesetzte Wasser und die leicht flüchtigen Komponenten im wesentlichen im Kopfstrom enthalten sind.
- 5 8. Verfahren nach Anspruch 7, **dadurch gekennzeichnet, dass** die Einleitung des Reaktionsgemisches aus dem Vorreaktor (13) in die Reaktiv-Destillationskolonne (15) an einem Punkt unterhalb der Katalysatorzonenmitte oder unterhalb in geringem Abstand zur Katalysatorzone erfolgt.
9. Verfahren nach Anspruch 7 oder 8, **dadurch gekennzeichnet, dass** der Kopfstrom einer weiteren Trennstufe, vorzugsweise einer Destillations- oder Extraktionskolonne, zugeführt wird, in welcher das Gemisch weiter aufgetrennt wird.
- 10 10. Verfahren nach einem der Ansprüche 1 bis 9, **dadurch gekennzeichnet, dass** die Reaktiv-Destillationskolonne (15) so gefahren wird, dass Carbonsäure und nicht umgesetztes Wasser im Sumpf der Reaktiv-Destillationskolonne (15) zurückbleiben.
11. Verfahren nach Anspruch 10, **dadurch gekennzeichnet, dass** die Einleitung des Reaktionsgemisches aus dem Vorreaktor (13) in die Reaktiv-Destillationskolonne (15) an einem Punkt oberhalb der Katalysatorzonenmitte oder oberhalb in geringem Abstand zur Katalysatorzone erfolgt.
- 20 12. Verfahren nach Anspruch 10 oder 11, **dadurch gekennzeichnet, dass** der Sumpfstrom der Reaktiv-Destillationskolonne (15) einer weiteren Trennstufe, vorzugsweise einer Destillations- oder Extraktionskolonne, zugeführt wird, in welcher das Gemisch weiter aufgetrennt wird.
- 25 13. Verfahren nach einem der Ansprüche 1 bis 12, **dadurch gekennzeichnet, dass** der Kopfstrom und der Sumpfstrom der Reaktiv-Destillationskolonne (15) einer weiteren Trennstufe, vorzugsweise je einer Destillations- oder Extraktionskolonne, zugeführt werden, in welcher das jeweilige Gemisch weiter aufgetrennt wird.
- 30 14. Verfahren nach einem der Ansprüche 1 bis 13, **dadurch gekennzeichnet, dass** das Verfahren kontinuierlich betrieben wird, d.h. der Carbonsäureester und das Wasser, resp. ein Gemisch derselben, werden kontinuierlich in den Vorreaktor (13) geleitet und das resultierende Reaktionsgemisch kontinuierlich aus dem Vorreaktor (13) abgezogen und in die Reaktiv-Destillationskolonne (15) geleitet, wo nicht-reagierter Carbonsäureester grösstenteils in seine Hydrolyseprodukte umgesetzt wird, wobei die Hydrolyseprodukte kontinuierlich als Kopfstrom oder als Sumpfstrom abgezogen und ggf. einer weiteren Trennstufe zugeführt werden.
- 35 15. Verfahren nach einem der Ansprüche 1 bis 13, **dadurch gekennzeichnet, dass** die Esterverbindung ein Methyl-, Ethyl-, i- oder n-Propylester, i- oder n-Butylester, insbesondere deren Acetate, oder ein Gemisch der vorerwähnten Esterverbindungen ist.
- 40 16. Verwendung einer Hydrolysis- und Trennungseinrichtung mit wenigstens einer Reaktiv-Destillationskolonne (15), insbesondere zum Umsetzen eines Carbonsäureesters in die entsprechende Carbonsäure und den entsprechenden Alkohol und wenigstens teilweisen Trennung der Hydrolyseprodukte in Einzelkomponenten, mit:
  - 45 - wenigstens einem Vorreaktor (13) mit wenigstens einem Ein- und einem Auslass zum Zu- resp. Abführen eines den Carbonsäureester aufweisenden Fluidstromes in den Vorreaktor (13) resp. aus diesem heraus,
  - einen ersten Katalysator, welcher im Vorreaktor (13) angeordnet oder aufgeschüttet ist;
  - ersten Heizmitteln (55) zum Heizen des Fluidstromes oder des Vorreaktors (13).
  - einer Reaktiv-Destillationskolonne (15) mit einem Einlass (23), welcher mittels einer Verbindungsleitung (17) mit dem Auslass (21) des Vorreaktors (13) verbunden ist, wobei die Reaktiv-Destillationskolonne (15) folgende Merkmale aufweist
  - 50 - eine einen zweiten Katalysator aufweisende Katalysatorzone (27) und wenigstens eine Rektifikationszone (29 oder 31), welche durch eine Destillationspackung, Raschigringen, Trennböden oder dergleichen gebildet ist;
  - am Destillationskolonnenkopf resp. Destillationskolonnenfuss angeschlossene Leitungen (37,35) zum Abziehen eines Kopfstromes resp. eines Sumpfstromes; und
  - 55 - zweite Heizmittel (41) zum Heizen des Sumpfes der Reaktiv-Destillationskolonne (15) zur hydrolytischen Gewinnung einer Carbonsäure und Alkohol aus dem entsprechenden Carbonsäureester und Wasser gemäss einem der Ansprüche 1 bis 15

17. Verwendung nach Anspruch 16, **dadurch gekennzeichnet, dass** der Vorreaktor (13) ungefähr vertikal angeordnet ist, wobei der Einlass (19) oben und der Auslass (21) unten oder umgekehrt der Auslass (21) oben und der Einlass (19) unten angeordnet ist.
- 5 18. Verwendung nach Anspruch 16 oder 17, **dadurch gekennzeichnet, dass** zwei Vorreaktoren (13a, 13b) oder ein Vorreaktor (13) mit zwei Reaktionskammern eingesetzt sind und Mittel vorgesehen sind, um den Zustrom jeweils durch einen der Vorreaktoren resp. eine der Reaktionskammern leiten zu können, sodass der jeweils andere Vorreaktor (13) resp. die andere Reaktionskammer mit frischem Katalysator beschickt werden kann.
- 10 19. Verwendung nach einem der Ansprüche 16 bis 18, **dadurch gekennzeichnet, dass** die Reaktiv-Destillationskolonne (15) eine Katalysatorzone (27) und eine untere und eine obere Rektifikationszone (29) resp. (31) aufweist, wobei die obere Rektifikationszone (31) oberhalb der Katalysatorzone (27) und die untere Rektifikationszone (29) unterhalb der Katalysatorzone (27) angeordnet ist.
- 15 20. Verwendung nach einem der Ansprüche 16 bis 19, **dadurch gekennzeichnet, dass** der Einlass an der Reaktiv-Destillationskolonne (15) sich im Bereich der Katalysatorzone (27) befindet.
21. Verwendung nach einem der Ansprüche 16 bis 20, **dadurch gekennzeichnet, dass** der Vorreaktor (13) rohrförmig ist, und der erste Katalysator eine Schüttung eines festen Katalysators ist.
- 20 22. Verwendung nach einem der Ansprüche 16 bis 21, **dadurch gekennzeichnet, dass** wenigstens der zweite Katalysator als strukturierte Katalysatorpackung ausgebildet ist.
23. Verwendung nach einem der Ansprüche 16 bis 22, **dadurch gekennzeichnet, dass** die strukturierte Katalysatorpackung durch Hohlräume aufweisende Packungselemente gebildet ist, wobei das Katalysatormaterial in die Hohlräume eingebracht ist.
- 25 24. Verwendung nach einem der Ansprüche 16 bis 23, **dadurch gekennzeichnet, dass** erster und zweiter Katalysator saure Feststoffkatalysatoren, z.B. Ionentauscherharze, sind, wobei der erste Katalysator eine Korngrösse zwischen ungefähr 0.35 und 3 mm und der zweite Katalysator eine solche zwischen ungefähr 0.5 und 1.5 mm, vorzugsweise 0.63 und 1 mm und ganz besonders bevorzugt zwischen 0.7 und 1 mm.
- 30

#### Revendications

- 35 1. Procédé pour obtenir par hydrolyse un acide carboxylique et de l'alcool à partir du carboxylate correspondant et d'eau, dans lequel procédé un courant contenant du carboxylate est amené en contact avec un catalyseur d'hydrolyse en présence d'eau à température élevée dans une colonne de distillation réactive (15), au moyen de laquelle le carboxylate est au moins partiellement hydrolysé dans l'acide carboxylique et l'alcool, et le mélange de réaction résultant est séparé simultanément au moins partiellement en composants dans la colonne de distillation réactive, les composés plus volatils, par exemple, l'alcool, étant extraits en tête de colonne de distillation réactive (15) sous la forme d'un courant dit de tête et les composés moins volatils, par exemple acide carboxylique, se rassemblant au moins partiellement dans le pied de colonne (15) sous la forme d'une fraction de fond, qui peuvent être extraits sous la forme d'un courant de pied de colonne ou de fond, **caractérisé en outre en ce que**
- 40 - le courant contenant le carboxylate est d'abord envoyé vers un pré-réacteur (13), dans lequel le carboxylate est amené en contact avec un premier catalyseur en présence d'eau, au moyen duquel le carboxylate est partiellement décomposé en produits d'hydrolyse ;
- 45 - le mélange de réaction est extrait du pré-réacteur (13) et au moins partiellement envoyé dans la colonne de distillation réactive (15), et est amené en contact avec un second catalyseur d'hydrolyse pour au moins une conversion partielle du carboxylate restant en acide carboxylique et en alcool.
- 50 2. Procédé selon la revendication 1, **caractérisé en ce qu'**au moins le courant de tête de la colonne de distillation réactive (15) ou le courant de pied de colonne est fourni à au moins un autre étage de séparation, et est au moins partiellement séparé en composants.
- 55 3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** le carboxylate est mélangé avec au moins une

quantité équimolaire d'eau, et en ce que le mélange carboxylate/eau est envoyé dans le pré-réacteur (13).

4. Procédé selon l'une des revendications 1 à 3, **caractérisé en ce que** le rapport molaire de carboxylate et d'eau est entre approximativement 1:1 et 1:15, de préférence entre 1:2 et 1:10, et plus particulièrement de préférence entre 1:4 et 1:7 ou 1:3 et 1:5, respectivement.
5. Procédé selon l'une des revendications 1 à 4, **caractérisé en ce que** le mélange carboxylate/eau est chauffé à une température comprise entre 30 et 100 °C, de préférence de 40 à 90 °C, et plus particulièrement de préférence entre 50 et 80 °C.
6. Procédé selon l'une des revendications 1 à 5, **caractérisé en ce que** le mélange de réaction en provenance du pré-réacteur (13) est envoyé dans la colonne de distillation réactive (15) dans la région où le catalyseur est disposé.
7. Procédé selon l'une des revendications 1 à 6, **caractérisé en ce que** la colonne de distillation réactive (15) est mise en fonctionnement de telle manière que l'eau n'ayant pas réagi et les composants volatils sont essentiellement contenus dans le courant de tête.
8. Procédé selon la revendication 7, **caractérisé en ce que** le mélange de réaction en provenance du pré-réacteur (13) est introduit dans la colonne de distillation réactive (15) à un point situé en dessous du centre de la zone du catalyseur ou à une faible distance en dessous de la zone du catalyseur.
9. Procédé selon la revendication 7 ou 8, **caractérisé en ce que** le courant de tête est fourni à un autre étage de séparation, de préférence une colonne d'extraction ou de distillation, dans laquelle le mélange est en outre séparé.
10. Procédé selon l'une des revendications 1 à 9, **caractérisé en ce que** la colonne de distillation réactive (15) fonctionne de telle manière que l'acide carboxylique et l'eau n'ayant pas réagi restent dans le pied de la colonne de distillation réactive (15).
11. Procédé selon la revendication 10, **caractérisé en ce que** le mélange de réaction en provenance du pré-réacteur (13) est introduit dans la colonne de distillation réactive (15) à un point situé au-dessus du centre de la zone du catalyseur ou à une faible distance au-dessus de la zone du catalyseur.
12. Procédé selon la revendication 10 ou 11, **caractérisé en ce que** le courant de pied de colonne de distillation réactive (15) est fourni à un autre étage de séparation, de préférence une colonne d'extraction ou de distillation, dans laquelle le mélange est en outre séparé.
13. Procédé selon la revendication 1 à 12, **caractérisé en ce que** le courant de tête et le courant de pied de colonne de distillation réactive (15) sont fournis à un autre étage de séparation, de préférence une colonne d'extraction ou de distillation chacun, dans laquelle le mélange respectif est en outre séparé.
14. Procédé selon l'une des revendications 1 à 13, **caractérisé en ce que** le procédé fonctionne en continu, c'est-à-dire que le carboxylate et l'eau ou un mélange de ceux-ci sont respectivement envoyés en continu dans le pré-réacteur (13), et le mélange de réaction résultant est extrait en continu du pré-réacteur (13) et envoyé dans la colonne de distillation réactive (15), où le carboxylate n'ayant pas réagi est, pour la majeure partie, converti en ses produits d'hydrolyse, les produits d'hydrolyse étant extraits en continu sous la forme d'un courant de tête ou sous la forme d'un courant de pied de colonne, et facultativement fourni à un autre étage de séparation.
15. Procédé selon l'une des revendications 1 à 13, **caractérisé en ce que** le composé ester est un méthyl, éthyl, i- ou n-propyl ester, i- ou n-butyl ester, spécialement des acétates de ceux-ci, ou un mélange des composés ester précités.
16. Utilisation d'un dispositif de séparation et d'hydrolyse ayant au moins une colonne de distillation réactive (15), en particulier, pour convertir un carboxylate en acide carboxylique correspondant et en alcool correspondant et au moins une séparation partielle des produits d'hydrolyse en composants individuels, ayant :
  - au moins un pré-réacteur (13) ayant au moins une entrée et une sortie pour fournir et décharger respectivement un courant fluide comprenant le carboxylate, respectivement, dans le pré-réacteur (13) et à partir de celui-ci ;

- un premier catalyseur, qui est disposé ou déposé dans le pré-réacteur (13) ;
- un premier moyen de chauffage (55) pour chauffer le courant fluide ou le pré-réacteur (13) ;
- 5 - une colonne de distillation réactive (15) ayant une entrée (23), qui est raccordée au moyen d'une conduite de raccordement (17) à la sortie (21) du pré-réacteur (13), la colonne de distillation réactive (15) ayant les caractéristiques suivantes :
- 10 - une zone du catalyseur (27) comprenant un second catalyseur et au moins une zone de rectification (29 ou 31), qui est formée d'un garnissage de distillation, d'anneaux de Rashig, d'étages de séparation ou similaires ;
- des conduites (37, 35), raccordées respectivement à la tête de la colonne de distillation et au pied de la colonne de distillation, pour extraire respectivement un courant de tête et un courant de pied de colonne ; et
- 15 - un second moyen de chauffage (41) pour chauffer le pied de la colonne de distillation réactive (15), pour obtenir par hydrolyse un acide carboxylique et de l'alcool à partir du carboxylate correspondant et d'eau suivant l'une des revendications 1 à 15.
- 17. Utilisation selon la revendication 16, **caractérisée en ce que** le pré-réacteur (13) est disposé approximativement verticalement, l'entrée (19) étant disposée au niveau de la partie supérieure et la sortie (21) au niveau de la partie inférieure ou, réciproquement, la sortie (21) étant disposée au niveau de la partie supérieure et l'entrée (19) au niveau de la partie inférieure.
- 18. Utilisation selon la revendication 16 ou 17, **caractérisée en ce que** deux pré-réacteurs (13a, 13b) ou un pré-réacteur (13) ayant deux chambres de réaction sont ou est utilisé(s), et **en ce que** des moyens sont prévus pour rendre possible la distribution du courant d'alimentation respectivement dans l'un des pré-réacteurs ou dans l'une des chambres de réaction, de sorte que l'autre pré-réacteur (13) ou l'autre chambre de réaction peut être approvisionné(e), respectivement, en catalyseur frais.
- 19. Utilisation selon l'une des revendications 16 à 18, **caractérisée en ce que** la colonne de distillation réactive (15) a une zone du catalyseur (27) et, respectivement, une zone de rectification inférieure et une supérieure (29) et (31), la zone de rectification supérieure (31) étant disposée au-dessus de la zone du catalyseur (27) et la zone de rectification inférieure (29) étant disposée en dessous de la zone du catalyseur (27).
- 20. Utilisation selon l'une des revendications 16 à 19, **caractérisée en ce que** l'entrée de la colonne de distillation réactive (15) est placée dans la région de la zone du catalyseur (27).
- 21. Utilisation selon l'une des revendications 16 à 20, **caractérisée en ce que** le pré-réacteur (13) est tubulaire, et **en ce que** le premier catalyseur est un lit d'un catalyseur solide.
- 22. Utilisation selon l'une des revendications 16 à 21, **caractérisée en ce qu'**au moins le second catalyseur est formé comme garnissage de catalyseur structuré.
- 23. Utilisation selon l'une des revendications 16 à 22, **caractérisée en ce que** le garnissage de catalyseur structuré est formé par des éléments de garnissage ayant des cavités, le matériau catalyseur étant introduit dans les cavités.
- 24. Utilisation selon l'une des revendications 16 à 23, **caractérisée en ce que** le premier et le second catalyseurs sont des catalyseurs solides acides, par exemple, des résines échangeuses d'ions, le premier catalyseur ayant une taille de particules comprise entre approximativement 0,35 et 3 mm et le second catalyseur ayant une taille de particules entre approximativement 0,5 et 1,5 mm, de préférence, 0,63 et 1 mm, et plus particulièrement de préférence entre 0,7 et 1 mm.



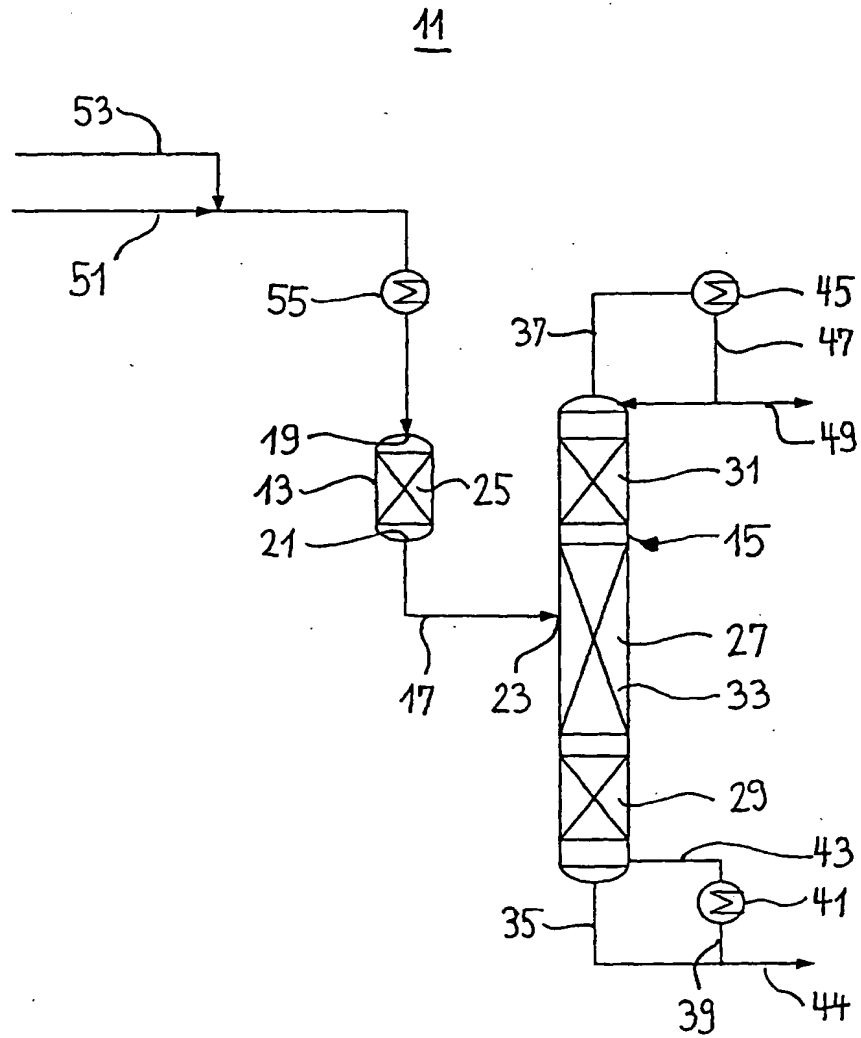


Fig. 1

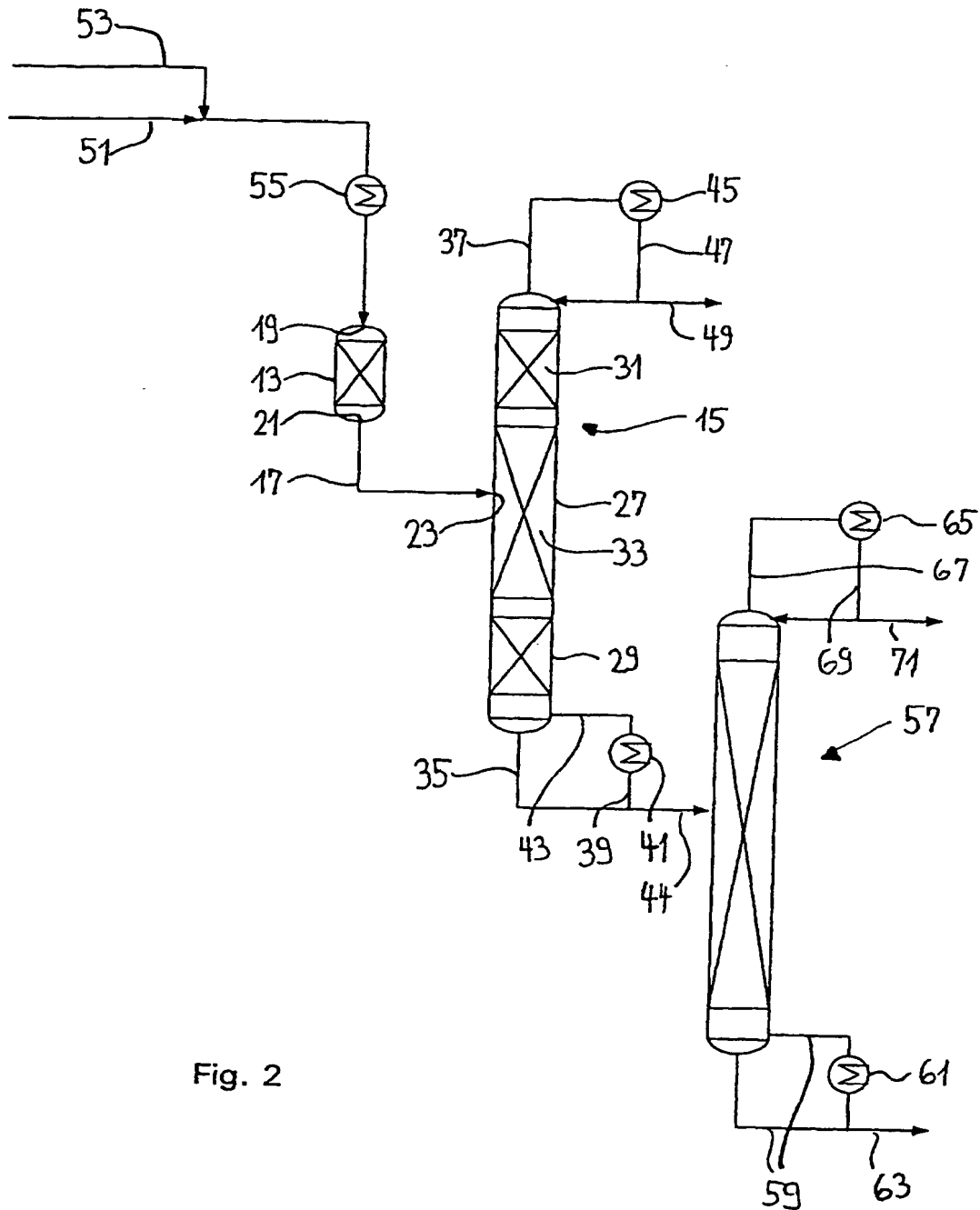


Fig. 2

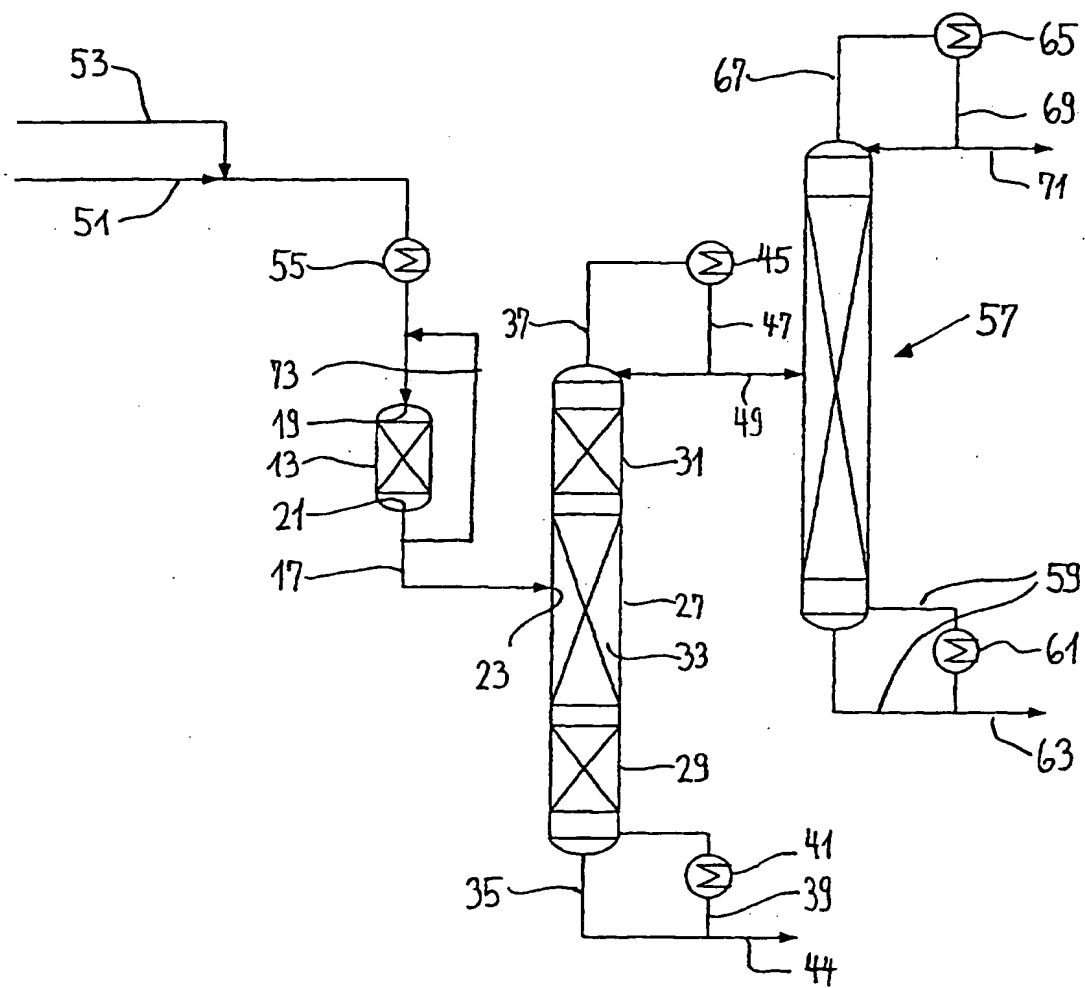


Fig. 3

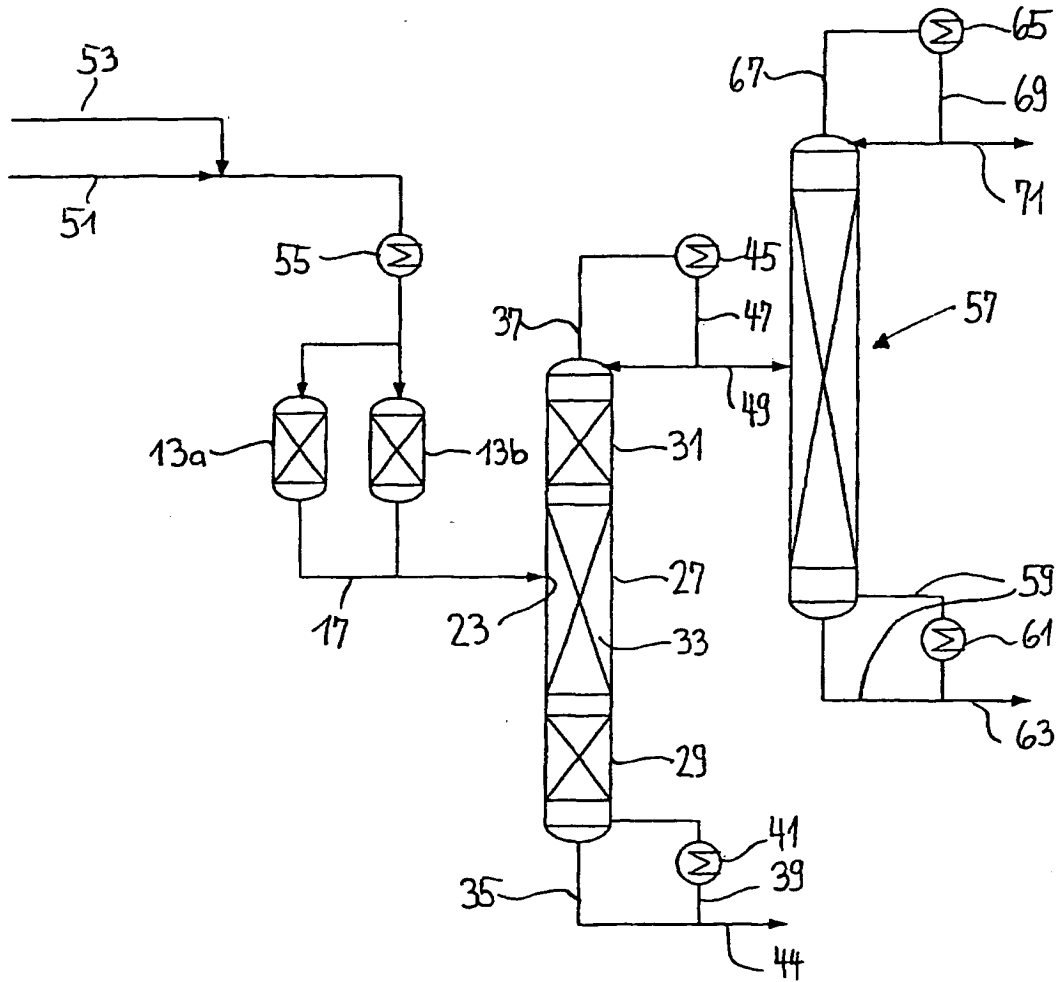


Fig. 4

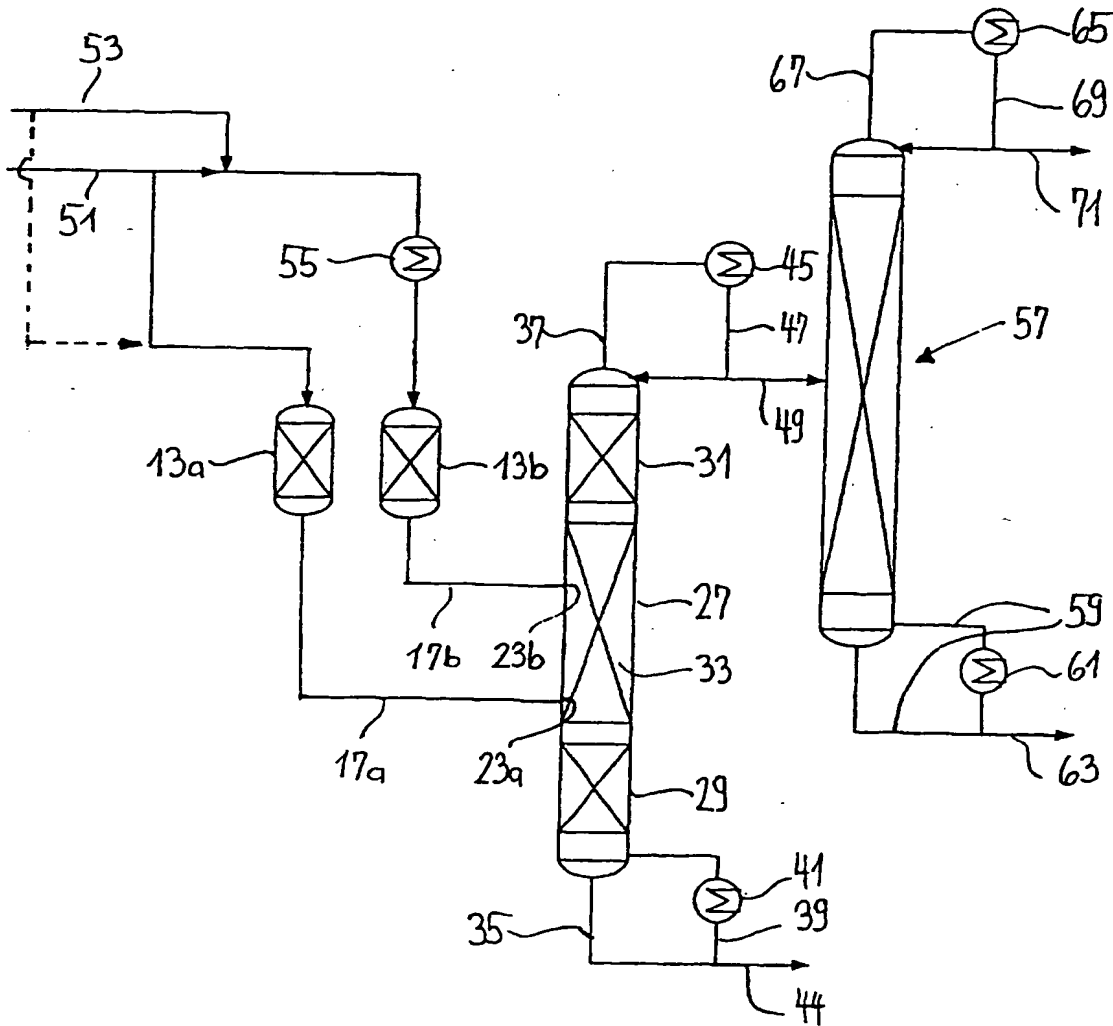


Fig. 5

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